

January 30, 2007

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Re: NREL Subcontract #ADJ-1-30630-12  
D.5.7

Dear Bolko,

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of August 16, 2006 to September 15, 2006, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS-based solar cells).

## **TASK 2: CuInSe<sub>2</sub>-BASED SOLAR CELLS**

### **Cu(InGa)(SeS)<sub>2</sub> Formation by H<sub>2</sub>Se/H<sub>2</sub>S Reaction**

We have previously characterized a sequential selenization/sulfization reaction of metallic Cu-In-Ga precursors for the formation of Cu(InGa)(SeS)<sub>2</sub> films [1]. This included characterization of the reaction pathways in single-reaction selenization and sulfization processes and composition profile development in the two-reaction processes in which sputtered Cu<sub>0.8</sub>G<sub>0.2</sub> / In precursors were reacted in H<sub>2</sub>Se for either 15 or 30 m at 450°C, followed by reaction in H<sub>2</sub>S at 550°C for either 15 or 30 m. Samples selenized for 15 minutes exhibited uniform Ga through the depth of the film, while those selenized for 30 minutes exhibited the commonly observed back-contact Ga accumulation which leads to low V<sub>OC</sub>. All films had a steep sulfur gradient near the front surface. With the films reacted at 450°C for 15 m in H<sub>2</sub>Se devices with V<sub>OC</sub> > 600 mV with  $\eta$  > 13% were demonstrated.

In this work, we characterize device performance as a function of variations in the two-step reaction. Results are summarized in Table I. A baseline with 15 m / 450°C for the H<sub>2</sub>Se and 15 m / 550°C for the H<sub>2</sub>S reactions yielded similar composition to that previously reported with [Ga]/[In+Ga] = 0.2 and [S]/[Se+S] = 0.4 as measured by EDS. Device performance was also similar with V<sub>OC</sub> = 0.65V and  $\eta$  = 12.6% so the benefits of the Ga incorporation were realized in V<sub>OC</sub>. Process variations investigated include:

1. An increase in H<sub>2</sub>S reaction time to 20 m resulted in similar [Ga]/[In+Ga] but lower FF and J<sub>SC</sub> in the devices (samples 1097.32a and 1102.11d). This could be

due to an interface collection barrier caused by too much S diffused into the Cu(InGa)(SeS)<sub>2</sub> surface. Symmetric XRD and EDS are not very sensitive to a surface S layer and GIXRD measurements to characterize the near surface of the Cu(InGa)(SeS)<sub>2</sub> have not been completed.

2. An increase in H<sub>2</sub>Se time to 30 minutes gave much lower [Ga]/[In+Ga], as reported previously, attributed to more complete reaction and consumption of the Cu<sub>9</sub>Ga<sub>4</sub> phase during selenization [1]. In addition, this leads to films with poor adhesion at the Mo/Cu(InGa)(SeS)<sub>2</sub> interface and most attempts to make devices resulted in delamination after film reaction or during CdS bath deposition. On one sample, devices were completed and had lower V<sub>OC</sub> consistent with the low Ga composition (sample 1097.21c).
3. Reducing the H<sub>2</sub>Se reaction time to 10 m gave a small increase in V<sub>OC</sub> but even lower J<sub>SC</sub> (sample 1102.21d).
4. Reaction in H<sub>2</sub>Se at lower T = 400°C was investigated to determine if it might give better uniformity (see June 2006 report under this contract). With reaction time increased to 45 m, comparable results for composition and device performance were obtained (sample 1102.12a) but visual non-uniformities remained.

In conclusion, the two-step reaction reproducibly enables the Ga to be uniformly incorporated and V<sub>OC</sub> > 0.62V to be attained. However, higher cell performance may require more precise optimization of the reaction conditions to optimize the S gradient and the current collection.

Table I. Reaction parameters, composition ratio measured by EDS, and device results for Cu(InGa)(SeS)<sub>2</sub> formed by two-step H<sub>2</sub>Se/H<sub>2</sub>S reactions.

| Sample # | H <sub>2</sub> Se |            | H <sub>2</sub> S |        | EDS    |        |      | $\eta$ (%) | V <sub>OC</sub> (V) | J <sub>SC</sub> (mA/cm <sup>2</sup> ) | FF (%) |
|----------|-------------------|------------|------------------|--------|--------|--------|------|------------|---------------------|---------------------------------------|--------|
|          | t (m)             | T (°C)     | t (m)            | T (°C) | Cu/III | Ga/III | S/VI |            |                     |                                       |        |
| 1102.22a | 15                | 450        | 15               | 550    | 0.87   | 0.20   | 0.36 | 12.6       | 0.643               | 28.9                                  | 67.8   |
| 1097.32a | 15                | 450        | 30               | 550    | 0.87   | 0.21   | 0.50 | 10.6       | 0.648               | 26.9                                  | 61.0   |
| 1102.11d | 15                | 450        | 30               | 550    | 0.90   | 0.18   | 0.37 | 8.7        | 0.621               | 26.7                                  | 52.6   |
| 1102.21d | <b>10</b>         | 450        | 30               | 550    | 0.91   | 0.19   | 0.38 | 5.4        | 0.665               | 15.5                                  | 52.6   |
| 1097.21c | <b>30</b>         | 450        | 30               | 550    | 0.96   | 0.05   | 0.21 | 4.7        | 0.522               | 25.9                                  | 34.7   |
| 1102.12a | <b>45</b>         | <b>400</b> | 15               | 550    | 0.85   | 0.2    | 0.37 | 12.4       | 0.620               | 31.1                                  | 64.5   |

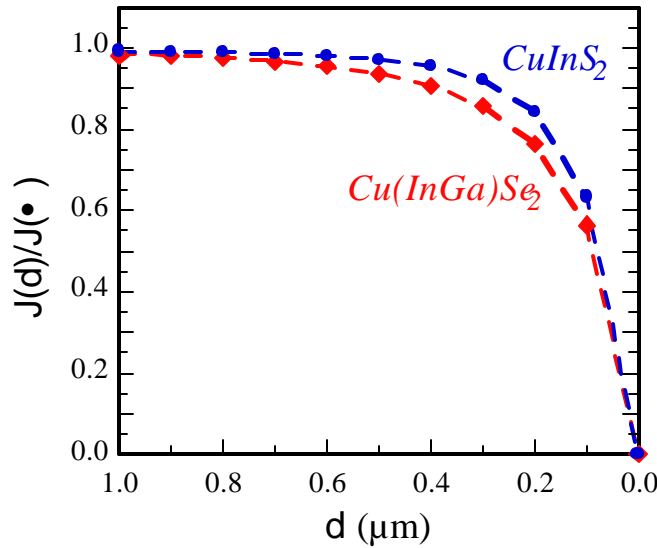
## Fundamental Materials and Interface Characterization

### *Cu(InGa)Se<sub>2</sub> Thickness*

We previously reported characterization of the effect of absorber layer thickness (d) on device behavior using Cu(InGa)Se<sub>2</sub> layers deposited with different times and also with an aqueous Br-etch to controllably reduce the thickness from 2.0 to 0.4  $\mu$ m [2]. Runs were repeated to test the reproducibility of the thinnest deposited layers. In the previous work, a 10 m deposition time to give thickness = 0.37  $\mu$ m gave a best cell with  $\eta$  = 7.8% with

$V_{OC} = 0.601$  V,  $J_{SC} = 20.7$  mA/cm<sup>2</sup>, and FF = 62.9%. A repeat run with the same deposition conditions and time gave thickness =  $0.38$   $\mu$ m and a best cell with  $\eta = 9.1\%$ ,  $V_{OC} = 0.544$  V,  $J_{SC} = 22.8$  mA/cm<sup>2</sup>, and FF = 73.6%. Repeat runs with 20 m deposition to give  $0.7$   $\mu$ m thickness gave comparable performance to that attained previously. Two conclusions can be made from this result. First, the reproducibility with the thinnest layers is worse than with thicker absorber layers. Second, cells with deposited thickness  $< 0.5$   $\mu$ m can be made with high FF. The only consistent loss with the thinnest Cu(InGa)Se<sub>2</sub> layers remains the loss in  $J_{SC}$ , which is expected due to incomplete absorption but is greater than predicted by device models [3,4].

Two approaches are being undertaken to increase  $J_{SC}$  in devices using absorber layers with thickness  $0.3 \leq d \leq 1.0$   $\mu$ m. First, methods will be developed to implement light scattering into Cu(InGa)Se<sub>2</sub> devices and determine its potential for increasing  $J_{SC}$ . The initial approach to this will be to investigate modifications to the deposition of ZnO or ITO and a sputter system will be fitted with the capability for controlled water vapor inclusion for this purpose. A second approach will be to determine if the higher absorption coefficient in CuInS<sub>2</sub> or S-containing alloys [5] can be used to increase  $J_{SC}$  with thin absorbers. Using the absorption coefficients measured by spectroscopic ellipsometer for evaporated Cu(InGa)Se<sub>2</sub> and CuInS<sub>2</sub> films [5], the relative loss in current due to incomplete absorption as a function of thickness was calculated and is shown in Figure 1. With  $d = 0.4$   $\mu$ m, 96 % of the incident light (above the  $E_g = 1.5$  eV) is absorbed in a CuInS<sub>2</sub> films while only 91% is absorbed in a Cu(InGa)Se<sub>2</sub> with  $E_g = 1.3$  eV.



**Figure 1. Relative loss in current due to incomplete optical absorption in CuInS<sub>2</sub> and Cu(InGa)Se<sub>2</sub> films.**

#### *Cu(InGa)Se<sub>2</sub>/Mo Back Contact*

Reaction of Mo with Se and/or S can cause adhesion problems at the back contact between Mo and Cu(InGa)(SeS)<sub>2</sub> after growth of absorber layers by reaction of Cu-Ga-In

precursors in hydride gases. Previously, sputtered Mo films on soda lime glass substrates were reacted in flowing  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{S}$ , or an equal mixture of the two (March 2006 report under this contract). In each case, the reaction was done at  $550^\circ\text{C}$  for 1 hour with a total hydride gas concentration of 0.35% in Ar. Characterization of the surface layers was done by XRD which showed  $\text{MoSe}_2$  for films reacted in  $\text{H}_2\text{Se}$  or  $\text{H}_2\text{Se}+\text{H}_2\text{S}$  and a much thinner  $\text{MoS}_2$  layer for a film reacted only in  $\text{H}_2\text{S}$ .

To further characterize the reaction of Mo with the hydride gases, XPS measurements have been done on films reacted under the same conditions. Results are shown in Table II. The surface compositions of the Mo reacted in  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{S}$  indicate the presence of  $\text{MoSe}_2$  and  $\text{MoS}_2$  respectively, as expected. The film reacted in equal parts  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{S}$  had no measurable S (above the detection limit of  $\sim 1\%$ ). It is also notable that Na was detected at the surface only after reaction with  $\text{H}_2\text{Se}$  or the mixed gas but not after reaction with  $\text{H}_2\text{S}$ .

To better understand the role of the thermodynamics in the reactions of Mo with S and Se the heats of formation ( $\Delta H_f$ ) of  $\text{MoSe}_2$  and  $\text{MoS}_2$  were calculated [6,7,8,9] and are summarized in Table III. Three cases are considered, reaction of  $\text{H}_2\text{X}$  with Mo, reaction of  $\text{X}_2$  with Mo or reaction of  $\text{H}_2\text{X}$  with  $\text{MoO}_2$  ( $\text{X} = \text{Se}$  or  $\text{S}$ ). While all the reactions to form  $\text{MoSe}_2$  or  $\text{MoS}_2$  have negative  $\Delta H_f$ , in each case, the heats of formation favor  $\text{MoS}_2$  over  $\text{MoSe}_2$ . Therefore, the result of Mo reacted with the  $\text{H}_2\text{Se}/\text{H}_2\text{S}$  mix cannot be explained by the equilibrium thermodynamics.

Table II. Summary of surface atomic percentages measured by XPS for reacted Mo substrates.

| Description                           | %C | %O | %Mo | %S | %Se | %Na |
|---------------------------------------|----|----|-----|----|-----|-----|
| Plain Mo                              | 22 | 48 | 31  | 0  | 0   |     |
| Mo reacted with $\text{H}_2\text{Se}$ | 48 | 22 | 9   | 0  | 19  | 2   |
| Mo reacted with $\text{H}_2\text{S}$  | 36 | 20 | 13  | 31 | 0   | 0   |
| Mo reacted with mix                   | 37 | 22 | 12  | 0  | 27  | 2   |

Table III. Heats of formation at 1 atm and 298.15 K for three different reactions forming  $\text{MoS}_2$  or  $\text{MoSe}_2$ .

| Reaction  | $\Delta H_f$ (kJ/mol) |
|---|-----------------------|
| $2\text{H}_2\text{S} + \text{Mo} \rightarrow \text{MoS}_2 + 2\text{H}_2$              | -235                  |
| $\text{Mo} + \text{S}_2 \rightarrow \text{MoS}_2$                                     | -405                  |
| $2\text{H}_2\text{S} + \text{MoO}_2 \rightarrow \text{MoS}_2 + 2\text{H}_2\text{O}$   | -131                  |
| $2\text{H}_2\text{Se} + \text{Mo} \rightarrow \text{MoSe}_2 + 2\text{H}_2$            | -181                  |
| $\text{Mo} + \text{Se}_2 \rightarrow \text{MoSe}_2$                                   | -377                  |
| $2\text{H}_2\text{Se} + \text{MoO}_2 \rightarrow \text{MoSe}_2 + 2\text{H}_2\text{O}$ | -76                   |

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Best regards,

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